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Measurement of the Chemical Species that Contribute to Urban Haze

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16. ABSTRACT

Measurements of the acidic (SO_2, HNO_3, and HNO_2) and basic (eg NH_3) gases that coexist with fine particles (<2.5 μm) are often used in models to determine the sources of species that contribute to the so-called urban haze. The measurement of these trace gaseous and particle contaminants by instrumental methods is often limited by instrumental sensitivity and by the interferences of other contaminates that coexist with the species of interest. An example of this problem is the measurement of NO_2 by chemiluminescence methods. For example, nitrogen containing species (eg HNO_2) can substantially interfere with the NO_2 measurements. In addition measurements of SO_2 and HNO_3 at concentrations <1ppb, even without the presence of the interferences, is difficult due to losses in the sampling inlet assemblies and/or the detection limit of the monitoring device. In this report we describe a new denuder system and denuder coating arrangement that eliminates interferences between oxides of nitrogen species and improves the reliability and precision of measurements of HNO_3 and HNO_2. We will also describe the physical properties and sampling characteristics of an annular denuder system tailored for visibility studies and present results of measurements made to demonstrate precision and accuracy of data obtained with the annular denuder system.

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MEASUREMENT OF THE CHEMICAL SPECIES THAT CONTRIBUTE TO URBAN HAZE

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Measurements of the acidic (SO_2, HNO_3, and HNO_2) and basic (eg NH_3) gases that coexist with fine particles (<2.5 μm) are often used in models to determine the sources of species that contribute to the so-called urban haze. The measurement of these trace gaseous and particle contaminants by instrumental methods is often limited by instrumental sensitivity and by the interferences of other contaminates that coexist with the species of interest. An example of this problem is the measurement of NO_2 by chemiluminescence methods. For example, nitrogen containing species (eg HNO_2) can substantially interfere with the NO_2 measurements. In addition measurements of SO_2 and HNO_3 at concentrations <1ppb, even without the presence of the interferences, is difficult due to losses in the sampling inlet assemblies and/or the detection limit of the monitoring device. In this report we describe a new denuder system and denuder coating arrangement that eliminates interferences between oxides of nitrogen species and improves the reliability and precision of measurements of HNO_3 and HNO_2. We will also describe the physical properties and sampling characteristics of an annular denuder system tailored for visibility studies and present results of measurements made to demonstrate precision and accuracy of data obtained with the annular denuder system.

INTRODUCTION

In most urban and non-urban atmospheres reduction of visual air quality has been attributed to air pollutants which scatter and absorb light. This resulting attenuation of light intensity may be expressed using the Beer-Lambert Law:

$$\text{Light transmittance} = I/I_o = \exp(-b_{ext} L) \qquad (1)$$

where I_o is the original light intensity, I is the light intensity after passing through a column of air length L and b_{ext} is the light extinction coefficient. The b_{ext} may be expressed as the sum of the scattering coefficients for gases (b_{sg}) and particles (b_{sp}), plus the absorption coefficients for gases (b_{ag}) (mainly NO_2) and particles (b_{ap}) (mainly elemental carbon or soot carbon) in the illuminated path between an observer and target.

In many urban atmospheres light scattering by fine particles (<2.5 μm in aerodynamic diameter) is the most significant factor that impact visual air quality. For example Dzubay and Clubb[1] showed that in the Research Triangle Park area of NC 77% of the b_{ext} was attributed to light scattering by fine particles. In Denver, CO, Lewis et al[2] found 65% of b_{ext} was also attributable to b_{sp}.

The role of the light scattering and absorption of light by gases and particles in visibility reduction has been studied by a number of investigators over the past 10 years. Many of these visibility studies[3] have concentrated on obtaining ambient air measurements of the chemical and physical properties of a broad range of atmospheric pollutants in order to calculate their relative contribution to light attenuation. Air quality data have also been used[2] to estimate the contribution of selected pollution emission sources to visual air quality. Air quality data collected to calculate light extinction budgets can have large uncertainty[4] unless the appropriate sampling and/or monitoring systems are used to measure the important gases (e.g. NO_2) and particles (NO_3^-, $SO_4^=$) that impact visibility.

We will discuss in this report recent improvements in sampling and analysis of atmospheric aerosols and gases in order to better estimate the contribution of such species as NO_2^-, NO_3^-, NH_4^- and $SO_4^=$ to visibility. Specifically we will present air quality measurements made in Boise, ID using a newly developed annular denuder method (ADM) designed to collect ambient concentrations of HNO_2, HNO_3, SO_2, NH_3, $SO_4^=$ and NO_3^- for subsequent analysis. Modification in denuder coating procedures to eliminate interferences between HNO_2 and HNO_3 will be described. We will also discuss how ambient concentrations of HNO_2 may cause chemiluminescent NO_2 measurements and b_{ag} to be overestimated.

EXPERIMENTAL

Site Descriptions

Boise, ID. During winter of 1986-1987 air quality data and samples were collected at two primary monitoring sites (Fig. 1) as part of the Environmental Protection Agency's (EPA) Integrated Air Cancer Project[5]. One site was located in a city park (Elm Grove Park) in a residential neighborhood impacted by wood smoke emissions from numerous single family dwellings. The second primary site (Fire Station) was on top of a fire station adjacent to a major intersection. This site was used to examine the chemical characteristics of primary emission from vehicles.

Research Triangle Park, N.C. (RTP). During the winter of 1987-1988 experiments were performed with annular denuders on the roof of the EPA Annex. These experiments were performed to test the effect of denuder coatings on the collection of HNO_3, HNO_2 and SO_2.

Sampling Schedule. Annular denuder and aerosol samples were collected in Boise and Denver primarily over 12 hour sampling periods beginning at 7 AM and 7 PM in order to represent daytime and nighttime conditions. The sampling schedule at the RTP site was typically over 20-22 hour periods from 10 AM to 9 AM.

Inlet-Annular Denuder-Filter Pack Configuration

A coarse particle elutriator-impactor inlet rendered inert by a Teflon coating was the primary inlet assembly used in these ADM studies. Figure 2 shows the inlet-denuder-filter pack arrangement used in Boise. A 47 mm Nylosorb membrane filter followed the Teflon filter, to collect HNO_3 produced from the disassociation of NH_4NO_3 particles originally collected on the Teflon filter. The inlet design, denuder coating extraction and analysis methods, and operational procedures have been described by Vossler et al.[6] In the study at RTP, the denuders and impactor inlet were modified to incorporate a replaceable fritted glass impactor surface coated with either Dow Corning oil or mineral oil to prevent bounce of large particles into the denuders. This modification is shown in figure 2. The impactor inlet d_{50} cutpoints were 2.5 μm at the flow rates used in Boise and 2.1 μm for the RTP study.

The objective of the experiments performed in RTP was to decouple the collection of HNO_3 from HNO_2 by coating the first annular denuder with a 0.2% solution of NaF. Denuder 2 and 3 were coated with Na_2CO_3. In this configuration all HNO_3 is collected on the NaF denuder and HNO_2 is only collected on the Na_2CO_3 denuders. Results and implications of this denuder arrangement are discussed later in this report.

Summary of Sampling and Analysis Methods

Table I lists samplers and analysis procedures used to obtain data on the concentrations of major inorganic gases and aerosols measured in Boise and RTP. The annular denuders were extracted in 15 ml of distilled water and stored in a refrigerator in sealed plastic bottles. Extracts and filters were shipped to EPA, Research Triangle Park, NC and stored in a refrigerator prior to analysis. Filters from the ADM were sealed in plastic petri dishes and stored in a refrigerator with the denuder extracts. The filters were extracted in 10 ml Ion chromatographic (IC) Na_2CO_3 buffer solution in an ultrasonic bath just prior to IC analysis for NO_2^-, NO_3^- and $SO_4^=$ content.

RESULTS

Annular Denuder and Related Gas-Aerosol Data

Figure 3 is a summary of the means of daytime(AM) and nighttime(PM) data for HNO_2, SO_2, HNO_3, $SO_4^=$, NO_3^-, NO_x and mass for samples collected at the Elm Grove Park and Fire Station primary sites in Boise, The samples were collected between November 8, 1986 and February 2, 1987 and represent 30% of the samples collected in Boise. The complete set of results from the ADM will be reported elsewhere. These samples were collected to assist in receptor modeling studies to determine the origin of extractable organic matter (EOM) and origin of mutagenic properties of the EOM. For this wintertime study nitric acid was typically less than 0.5 $\mu g/m^3$ while the particle nitrate averaged 5 $\mu g/m^3$. This is contrasted to summertime studies

in the Eastern U.S. where nitric acid is typically 2 to 3 times the fine particle nitrate concentrations.[6]

Table II is a summary of the correlation statistics for data collected with the ADM systems, CO and NO_x monitors and dichotomous samplers operated at the two main monitoring sites in Boise. These correlations between key chemical air pollutant species serve as one means of evaluating and comparing air quality between the Fire Station and Elm Grove Sites in Boise. Also these correlations are used in identifying chemical species which may serve as candidates for use as tracers for receptor modeling calculations. For example, the high correlation between Pb and CO suggests CO may be a useful surrogate for Pb as a tracer for mobile source emission in receptor modeling calculations.

Table III are selected ADM results from the Elm Grove Site in Boise. These data are presented to provide information on the relative daytime-nighttime concentrations of gases and aerosols and show the variability in the amount of nitrate that evaporates from the ADM Teflon filters. The significance of this observation to visibility studies will be discussed later.

Precision and Accuracy of Sampling and Analysis Procedures

Two factors which are considered in estimating the precision of the measurements obtained with the denuder system are flow rate variations and precision of IC analysis. In the ADM study reported by Vossler et al[6] paired samples had average differences for the measurement of SO_2, HNO_3, and HNO_2 of 3.4%, 6.4% and 8.3%. These rather small deviations were due mainly to variations in sampling flow rate of the paired assemblies and ion chromatography analysis. Typically variations were less than ± 5% for flow and less than ± 3% for IC analysis. For our studies in Boise and RTP, NC the IC analysis precision for $SO_4^=$, NO_3^-, NO_3^- was typically better than ± 2%, and flows were maintained to ± 5%.

Sulfur-Sulfate Relationship

In Boise fine particle samples were collected with dichotomous samplers to obtain mass and elemental composition data by XRF procedures for use in receptor model calculations. The mass ratio of fine particle sulfate concentrations measured with the ADM to the sulfur measured from the dichotomous sampler by XRF for samples collected at both main monitoring sides in Boise was $SO_4^=$ (ADM)/S(XRF) = 2.99 ± 0.24 at the 95% confidence limits. This is in close agreement to the $SO_4^=$/S data obtained by Lewis et al[2] in a wintertime, 1982, visibility study in Denver. The ratio of 3.00 corresponds to all sulfur being in the form of sulfate. Figure 4 is a weighted least squares plot of $SO_4^=$ versus the S in fine particles sampled in Boise. In the weighted least square calculation[8] the data was forced through zero and data weighted so that the variance of Y ($SO_4^=$ concentration) was proportional to X^2 (X = S concentration). Thus the best estimate of the regression coefficient is the average of n slopes obtained from each pair of observations Y_i/X_i. A number of data points are below the best straight line fit of the data for sulfur concentrations >1.2 $\mu g\ m^{-3}$. This suggests the data may exist in two modes. Additional samples are being analyzed to determine whether this is real or due to other factors such as incomplete extraction of the $SO_4^=$ due to elevated concentrations of extractable organic matter present on the filters.

DISCUSSION

For studies performed in Boise and a previous Denver visibility study performed in 1982[2], a number of similarities in air quality data

were observed. For example, the mean concentration of nitrate in Boise was typically 13% of the fine particle mass (Figure 3). In the previous wintertime study in Denver[2] nitrate represented 14% of the daytime fine particle mass.

In Boise, HNO_2 concentrations averaged nearly 10% of the NO_2 values. For some periods, even during the day, the HNO_2 averaged 7% of the NO_2 concentration. During summer, HNO_2 daytime concentrations are typically less than 1 $\mu g/m^3$. However, during winter, cold and cloudy conditions tend to reduce the photo-disassociation of HNO_2, which may account for a mean daytime concentration of HNO_2 of 3 $\mu g/m^3$, observed in Boise (Figure 3). In addition, it should be noted chemiluminescent NO_x monitors respond to HNO_2 just as it responds to NO_2. Therefore, NO_2 measurements in Boise (and Denver) or any other urban area would tend to be overestimated due to the positive interference from HNO_2. This, in turn, would require adjustment in chemiluminescent NO_2 data in order to accurately calculate the contribution of NO_2 to the light extinction budget. For example on January 14, 1987 the average daytime HNO_2 concentration was 4.3 $\mu g/m^3$, which was 9.5% of the NO_2 concentration. Therefore the average daytime NO_2 concentration was really 40 $\mu g/m^3$ rather than the 45 $\mu g/m^3$ measured by the chemiluminescent NO_x monitor.

Table II and Figure 3 contain data that indicate that SO_2, nitrate, CO, Pb, fine particle mass and sulfate mean concentrations were nearly identical and correlated for data collected at the two primary monitoring sites in Boise. This indicates that air quality between the two sites was relatively homogeneous. This is an important observation, if calculations on pollutant exposure are to be performed using the data from these two primary monitoring sites.

For studies where light extinction budgets are to be calculated, data on not only the relative contribution of the various chemical species present in the fine particles are needed, but also data on the relative size distribution of these particles. Hasan and Dzubay[9] have shown that size distributions of S and Pb in Denver are significantly different. For example the sulfur peak concentration was in the optimum light scattering region (0.5 µm), while the Pb peak concentration was near 0.2 µm. The Hasan and Dzubay[9] study utilized a micro-orifice impactor to obtain size distribution data. Based on our studies in Boise, data on the size distribution and concentration of nitrate would appear to be important parameters that need to be measured to obtain reliable light extinction budgets. To obtain reliable size distribution of nitrate with the micro-orifice impactor (MOI), modification of the MOI sampling protocol is necessary. One modification that should be considered is an arrangement where a Na_2CO_3 coated annular denuder and impactor inlet precedes the entrance to the MOI. The impactor inlet removes large particles to minimize particle bounce and a Na_2CO_3 coated annular denuder removes HNO_3 and SO_2 to prevent interaction of reactive gases with the particles and/or collection surface at each stage of the MOI. The collection stages should be a thin membrane surface coated with a mixture of silicone oil and Na_2CO_3 to prevent evaporation of NH_4NO_3 after collection and particle bounce. Each stage is then extracted and the NO_3^- and $SO_4^=$ are measured by IC procedures. For studies where the relative contribution of $SO_4^=$ and NO_3^- to light scattering are to be obtained this protocol might be a viable method to obtain the needed data. Figure 5 is a diagram of the modified MOI arrangement which could be used in visibility studies to obtain mass and size distribution data for fine particle sulfate and nitrate.

To improve the reliability of HNO_3 and HNO_2 data obtained with the annular denuder, a modification of the annular denuder coating procedure was tested. In previous annular denuder studies some oxidation of HNO_2 to

nitrate on the denuder surface during sampling was possible during summertime conditions. Recently Febo et al[10] reported on the use of a NaCl coated denuder followed by Na_2CO_3 denuders to decouple the collection of HNO_3 from HNO_2. In this configuration only HNO_3 (and some SO_2) is collected on the NaCl coated denuder, and HNO_2 is collected on the Na_2CO_3 denuder. Thus if HNO_2 is oxidized on the Na_2CO_3 denuder there would be no interference with HNO_3 measurements since the HNO_3 had been removed by the NaCl coated denuder. In our laboratory we choose to use a NaF coated denuder instead of the NaCl because the Cl^- peak tended to obscure the NO_2^- and NO_3^- peaks during ion chromatographic analysis of the denuder extract. In our studies the first denuder is coated with 0.2% NaF. The coating procedure is identical to the procedure described by Vossler et al.[6] At this concentration 99.9% of the HNO_3 is collected on the NaF denuder at a flow rate of 10 L/minute along with some ambient SO_2. The amount of SO_2 collected on the NaF denuder appears to depend on relative humidity. There was no evidence of HNO_2 collection on the NaF coated denuder. The HNO_2 and balance of the ambient concentrations of SO_2 are found on the 1st Na_2CO_3 denuder. These preliminary studies suggest the annular denuder system using a NaF coated denuder followed by two Na_2CO_3 coated denuders eliminates the potential problem of HNO_2 interfering with HNO_3 measurements due to oxidation of NO_2^- to NO_3^- on the denuder.

Finally, examination of wintertime annular denuder data collected at a site 7 miles from downtown Denver indicated a high degree of variability in the amount of NO_3^- that evaporates from the Teflon filters. For example for 9 sampling periods in Denver in 1987 the % nitrate that evaporated from the Teflon filter and collected on the backup Nylon filter averaged 71%. Table III contains Boise ADM data and shows that a substantial amount of nitrate evaporation from ADM Teflon filters also occurs similar to the ADM results from Denver. In the studies performed by Vossler et al[6]) the evaporation of NO_3^- was attributed to changes in temperature and humidity. Due to high variability in the nitrate evaporation from the Teflon filters that can occur during sampling, particulate NO_3^- data from a nylon or Na_2CO_3 treated filter located downstream of the Teflon filter is necessary to obtain the true fine particle nitrate concentrations. However, the HNO_3 and particle nitrate data obtained with annular denuder systems would tend to be reliable due to the unique design of the sampler.

SUMMARY

Annular denuder and related air quality data collected in Boise, ID as part of the EPA Integrated Air Cancer indicated fine particle nitrate to be a major fraction (13%) of fine particle mass, while sulfate represented 5% of FP mass. Nitrous acid concentrations averaged 10% of NO_2 concentration and would produce a significant interference with chemiluminescent NO_2 determinations. Annular denuder data showed substantial evaporation of fine particle nitrate occurs from Teflon filters even during wintertime conditions. This suggests filter pack measurements of nitrate and HNO_3 may have substantial uncertainties. Introduction of a NaF annular denuder between the inlet and a Na_2CO_3 denuder eliminates the potential interference of HNO_2 with HNO_3 measurements and improves the annular denuder method as a tool to measure gas and aerosol phase oxides of nitrogen.

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Boise; Debbie Lovett and Dennis Williams of NSI for the analysis of ADM samples from Boise, ID and Denver, CO, Stella Mousmoules for typing the manuscript, J. Wu of NSI for assisting in the statistical analysis, C.W. Lewis and T.G. Dzubay for their critique of this report.

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Table I. Samplers and Analysis Procedures Used in Boise Study

Sampler/Analyzer	Flow Rate L min^{-1}	Species*	Ref.
Annular Denuder Method (ADM) (Boise, ID)	15	SO_2, NO_3, SO_4^{2-}, HNO_2 HNO_3	6
Annular Denuder Method (ADM) (RTP, NC)	10	SO_2, HNO_3, HNO_2, NO_3^-, SO_4^{2-}	6
Anderson Inc. Dichotomous Sampler	16	Mass, Elemental	7
Monitor Laboratories Chemiluminescent NO_x Analyzer	1	NO, NO_2, NO_x	
Beckman Gas Cell CO Monitor	1	CO	7

*47 mm Gelman Teflon filters followed by 47 mm Nylosorb filters were used with the ADM system; ADM system fabricated by University Research Glassware, Carrboro, NC. A pair of 37 mm Gelman Teflon filters were used to collect particles with the dichotomous sampler.

Table II. Summary of Correlation Statistics for Gas and Aerosol Samples Collected in Boise, ID

Species (Site)	N	AM	N	PM	N	Overall
HNO_2 vs NO_2 (EGP)	19	0.700	25	0.564	44	0.552
HNO_2 vs NO (EGP)	19	0.570	25	0.634	44	0.529
HNO_2 vs NO_2 (FS)	17	0.381	22	0.634	39	0.375
HNO_2 vs NO (FS)	17	0.610	22	0.858	39	0.557
Pb vs CO (EGP)	20	0.718	23	0.643	43	0.682
Pb vs CO (FS)	18	0.920	24	0.744	42	0.835

AM refers to data collected between 7 AM and 7 PM, PM refers to data collected between 7 PM and 7 AM.

Table III. Annular Denuder Method Data for Boise

DATE SAMPLED	TIME	Concentration, μg m^{-3} GASES HNO_2	GASES HNO_3	GASES SO_2	PARTICLES NO_3^-	PARTICLES $SO_4^=$	% Nitrate Found on Nylon Filter
12-6-86	night	6.95	0.0	5.40	1.68	1.16	30
12-7-86	day	2.00	0.25	2.55	2.40	2.04	81
12-7-86	night	5.35	0.03	6.66	1.46	1.88	25
12-9-86	night	3.29	0.16	10.53	3.05	1.39	56
12-10-86	night	3.83	0.12	9.66	4.32	2.12	26
12-11-86	day	1.37	0.34	7.60	4.70	2.08	40
12-11-86	night	7.52	0.09	12.03	4.46	2.91	14
12-12-86	day	2.79	0.20	10.62	4.14	2.41	29

Samples were collected between 7AM-7PM (day period) and 7PM-AM (night Period)

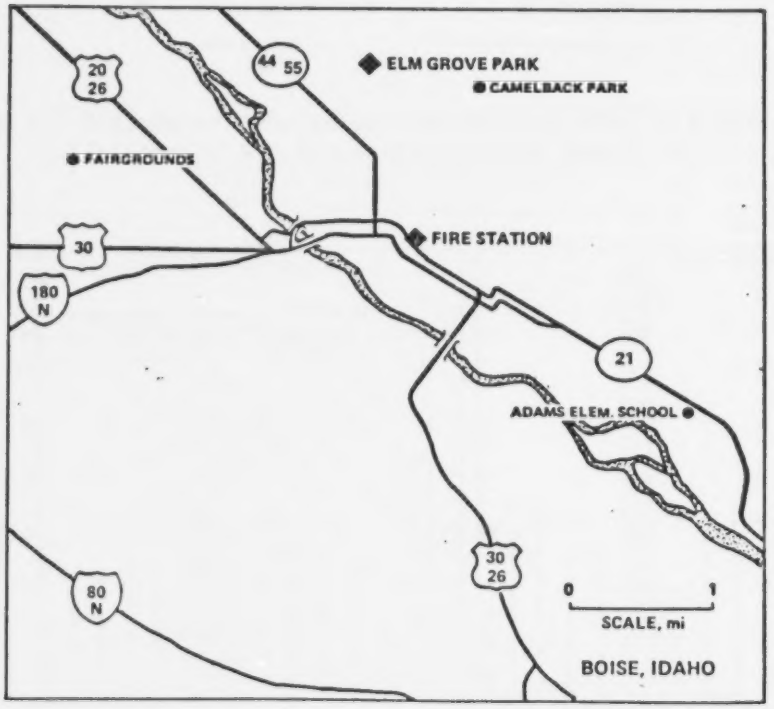

Figure 1 - Map of Boise, ID showing location of main and secondary monitoring sites used to collect air quality data in support of EPA's Integrated Air Cancer Project.

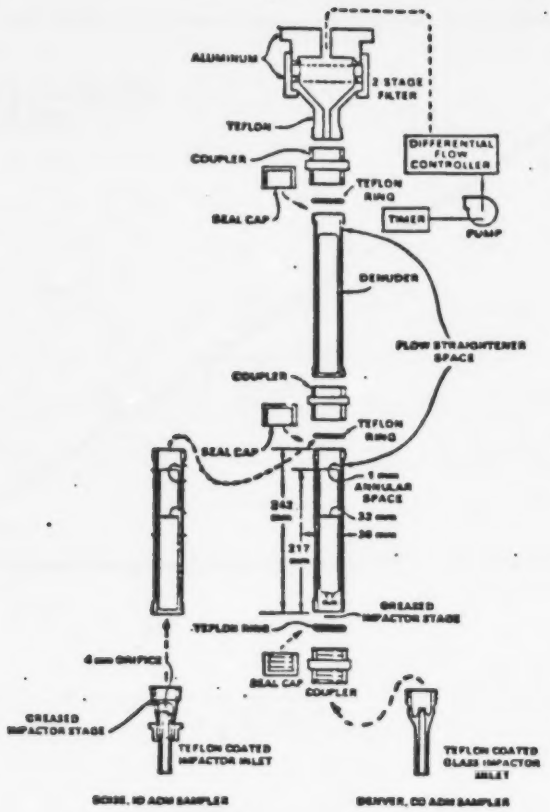

Figure 2 - Diagram of annular denuder systems used in the Boise, ID EPA's Integrated Air Cancer Project and Denver Air Toxic Study.

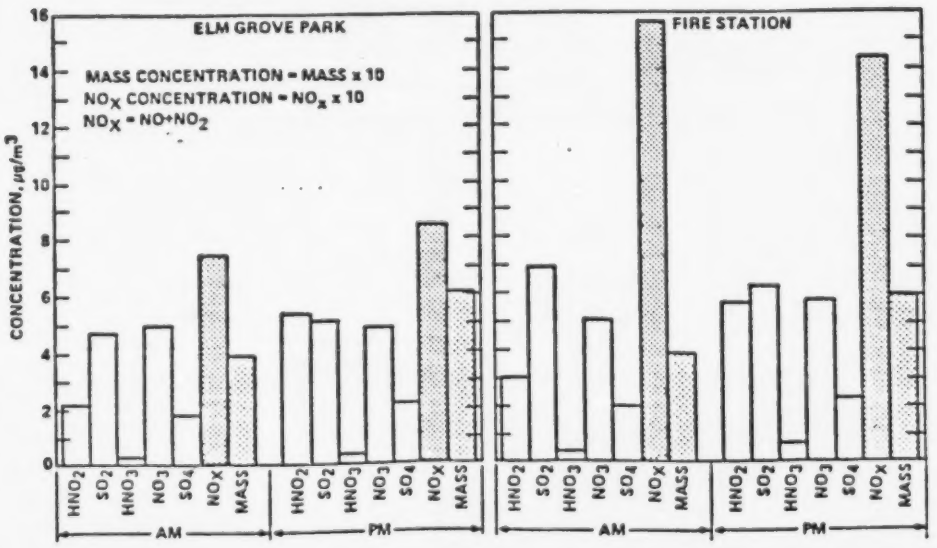

Figure 3 - Means of AM and PM measurements at the main monitoring sites in Boise, ID during the winter of 1986 and 1987.

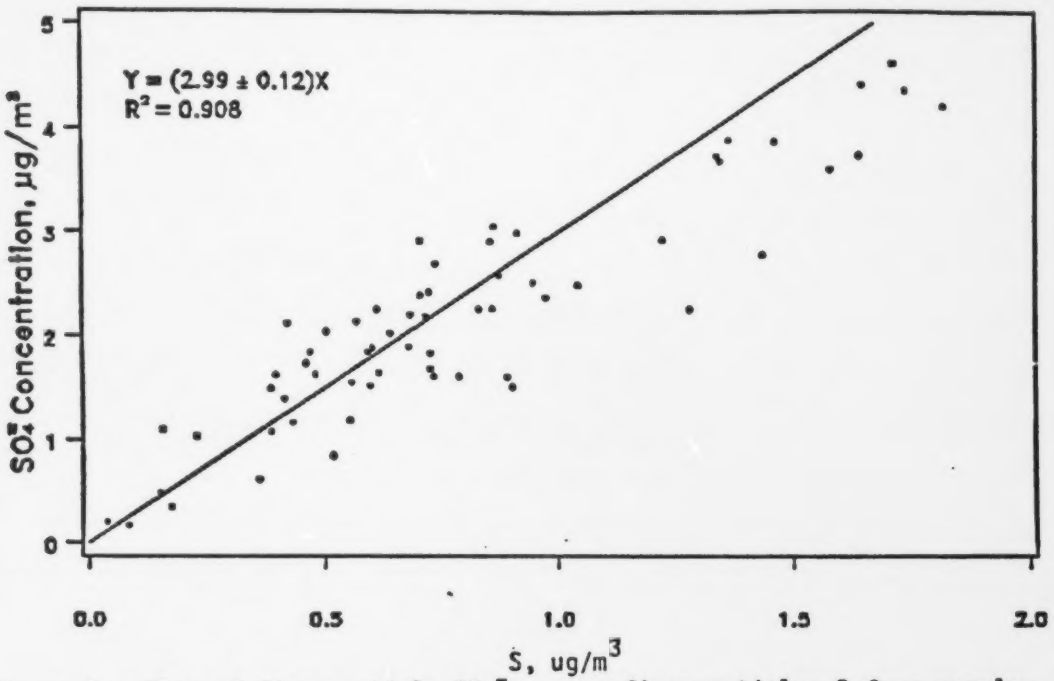

Figure 4 - Plot of fine particle $SO_4^=$ versus fine particles S from samples collected in Boise IACP study.

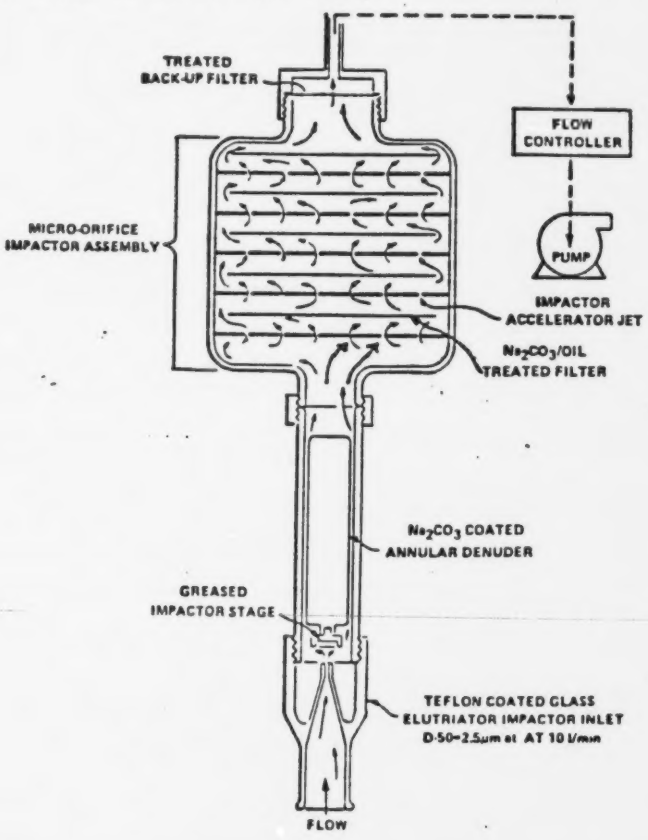

Figure 5 - SCHEMATIC OF IMPACTOR SAMPLER COUPLED TO ANNULAR DENUDER AND IMPACTOR INLET FOR USE IN VISIBILTIY STUDIES